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(54) **Dental restorative compositions having improved mechanical properties and hydrolytic stability**
Zahnersatzmaterialien mit verbesserten mechanischen Eigenschaften und Hydrolysestabilität
Compositions restauratives dentaires à propriétés mécaniques et stabilité à l'hydrolyse améliorées

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Description

The invention relates to a dental restorative composition having improved mechanical properties and hydrolytic stability.

Background of the invention

Dental restorative compositions comprising a polymerizable resinous composition plus a filler are finding wide acceptance in the practice of dentistry. An illustration of such compositions is the dental filling material described by Lee et al. in U.S. Patent No. 3,539,533. However, such resin based dental filling materials have found limited use for the filling of cavities on the grinding surfaces of molars. The reason for this is that such compositions have been found to have inadequate wearing properties to withstand the stresses which are normal in such areas. Among the factors that contribute to the inadequate wear properties of the prior art resinous dental restorative dental compositions are microfractures of the overall composite and debonding that occurs at the filler/polymer matrix interface. Both of these are most likely to occur during the cyclic loads encountered while chewing in an aqueous environment, with modest temperature fluctuations. Inadequate hydrolytic stability appears to contribute to both the microfractures and debonding. The present invention is directed to a dental restorative composition that substantially improves hydrolytic stability, resistance to debonding at the filler/polymer inter face, and resistance to the formation and propagation of microfractures in the composite.

Brief summary of the invention

The invention provides a dental restorative dental composition in accordance with claim 1.

Preferably, at least 70 to 100 percent of the particles of said filler have a size less than 5 μm , and most preferably the volume average particle size is not more than 5 μm .

In a preferred aspect, the composition of the invention contains from 5 to 30 weight per cent of colloidal silica, percentage being based upon the weight of the entire dental restorative composition.

The prior art

Dental restorative compositions that include a polymerizable resinous compound free of active hydrogen have been disclosed. For instance, see Orlowski et al., U.S. Patent No. 4,220,582, who disclose the use of the dimethacrylate of ethoxylated bisphenol-A and polyethylene glycol dimethacrylate in dental restorative compositions.

The use in dental restorative compositions of hydrophobic fillers such as quartz has been disclosed. For instance, see Schmitt et al. in U.S. Patent No. 3,923,740.

Ibsen et al., in U.S. Patent No. 4,297,266, disclose dental restorative compositions containing "hydrophobic" colloidal silica and 2 to 30 μm glass particles as fillers. Among the resins disclosed are ethoxylated bisphenol-A dimethacrylate and triethylene glycol dimethacrylate. US—A—3,792,531, contains a similar disclosure.

Dixon, in U.S. Patent No. 4,222,835, teaches polymerizable compositions (for coatings or fiber glass-reinforced materials) containing a wide variety of acrylic esters.

Lee et al., in U.S. Patent No. 4,032,504, disclose dental restorative compositions including a filler having a particle size of from 0.5 to 50 μm , with an average particle size of from 2 to 15 μm .

Dental restorative compositions containing sub- μm size fillers have also been disclosed. For instance, see Australian Patent No. 484,167.

Detailed description of the invention

In its broadest aspect, the invention provides a means to obtain a combination of a number of desirable features. First, the polymerizable compositions employed in the invention are relatively hydrophobic when cured, which enhances the hydrolytic stability of the restorative compositions. Second, relatively hydrophobic and chemically durable fillers are employed in order to provide additional resistance to hydrolytic attack at the filler/polymer matrix interface. And third, the use of small filler particles at relatively high filler loadings decreases the interparticle spacing in the cured composite which results in an increased number of obstacles to the propagation of small cracks initiated by defects in the system such as voids. In preferred aspects of the invention, the number of voids in the cured composite are reduced by employing relatively low viscosity resinous compounds, and/or by mixing the paste system under vacuum and preserving the resultant low void content by the use of a single component photocured system.

The various components of the invention, which are described more fully below, are employed for the purpose of achieving the above described features of the invention.

The polymerizable composition that is employed as the polymer matrix in the invention is a compound that has at least two olefinically unsaturated groups and which is relatively hydrophobic when cured, as is evidenced by low water absorption. One way to obtain the desired hydrophobic properties is to employ polymerizable compounds that are free of active hydrogen. By "active hydrogen" is meant the hydrogen contained in groups such as hydroxyl, carboxyl, primary or secondary amino, amido, sulfhydryl, and the like. (A convenient test for such active hydrogen groups is that they react with isocyanate in the presence of tertiary amine catalyst). A wide variety of such compounds can be employed. They include alkoxyated bisphenol-A acrylates or methacrylates, alkane diol acrylates or methacrylates, polyalkylene glycol acrylates or methacrylates and the like. The preferred compounds are the C₄—C₁₂ alkane diol acrylates or methacrylates such as 1,10 decamethylene diol dimethacrylate and 1,6-hexamethylene diol dimethacrylate, and ethoxyated bisphenol-A dimethacrylate. The nature and preparation of such compounds are known in the art.

The dental restorative composition of the invention includes a polymerization initiator. Such initiators are known in the art and can be used in their customary proportions. For instance, the composition can be divided, one package containing a peroxide such as benzoyl peroxide, and the other containing an activator for the peroxide such as N,N-di-(2-hydroxyethyl)-p-toluidine. Other initiator systems known in the art can also be used.

In order to minimize the formation of voids, in a preferred aspect of the invention, the initiator is a photosensitive initiator system so that the mixing step necessary for the two-component, self-curing composite systems can be avoided. In this aspect, a one-package system is used. Resin, filler, and the photosensitive initiator system are mixed under a vacuum to reduce void formation. The composition then needs no further mixing by the dentist or dental technician. Such photosensitive initiator systems include benzoin, benzoin ethers and esters, 2,2-diethoxy acetophenone, and the diketone compounds plus a reducing agent that are disclosed by Dart et al., in U.S. Patent No. 4,071,424. Specific examples of preferred photoinitiator systems include benzil and/or camphoroquinone plus N,N-dimethylaminoethyl methacrylate or ethyl 4-(N,N-dimethylamino)-benzoate.

The filler employed in the invention has a volume average particle size below 15 μm , and preferably, below 5 μm . Thirty per cent of the filler particles, and preferably 70 to 100 per cent, have a size below 5 μm . The filler is employed in an amount within the range of from 35 to 78 volume per cent, based on the volume of the filler plus the polymerizable composition. Thus, the filler is employed in relatively high proportions. A volume per cent of 35 to 78 corresponds approximately to 50 to 95 weight per cent of the dental restorative composition of the invention, depending on the specific gravity of the filler.

The hydrophobic, chemically durable fillers that are used are acid-washed and heat-treated barium or strontium glass. The hydrophobic fillers will absorb less than 0.1 weight per cent water (prior to addition of silane coupling agent) when exposed to normal ambient conditions. Water content of the filler is determined by a differential scanning calorimeter ("DSC"). The first departure from baseline in a DSC scan is caused by the presence of water. To determine the amount present, the area under the peak is determined and normalized relative to the weight of the sample.

The barium or strontium glass that may be employed as the filler is selected for chemical durability, as is evidenced by resistance to leaching in an aqueous environment. Such glasses are substantially free of alkali metal oxides, and are single phase glasses. If the mole per cent of barium or strontium oxide exceeds a certain point, the glass becomes two-phased. This proportion can vary, depending upon the presence and proportion of other metal oxides in the glass. For one preferred type of glass that is composed of oxides of barium, silicon, boron, and aluminum, the upper limit for a single phase glass is about 20 mole per cent barium oxide. One preferred glass for use in the invention has the following composition:

SiO ₂ —67	mole per cent
BaO—16.4	mole per cent
B ₂ O ₃ —10	mole per cent
Al ₂ O ₃ —6.6	mole per cent

The essential ingredients in the glass are the oxides of barium and/or strontium and silicon. Oxides of other metals such as aluminum and boron may also be present so long as such oxides do not detract from the chemical durability of the glass. Thus, significant quantities of alkali metal oxides should be avoided because, as is well known, alkali metal ions are quite soluble in aqueous media, and therefore will reduce the chemical durability of the glass. The minimum barium and/or strontium content of the glass is preferably that which is sufficient to impart x-ray opacity to the glass.

The barium and/or strontium glass powder used in the invention is acid washed and then subjected to a heat treatment to enhance its resistance to attack by water. The procedures are the following:

The acid-washing treatment to which the glass powder is subjected is carried out by known procedures. For instance, a mixture of 1 part (by weight) of glass powder, 1 part of 37 per cent aqueous hydrochloric acid, and 1 part of de-ionized water is stirred at room temperature for 45 minutes, filtered, and rinsed with de-ionized water until the pH of the filtrate is the same as the rinse water. The powder is then dried at about 50°C overnight in a forced air oven. The acid wash is used to remove metal impurities from the glass, and to reduce the amount of leachable barium or strontium from the surface of the glass.

The acid-washed glass powder is subjected to a heat treatment to reduce the affinity of the glass powder for water. This heat treatment is carried out at an elevated temperature below the sintering temperature of the glass powder (the

sintering temperature can be determined by known procedures, as by thermo-mechanical analysis (TMA), but high enough to cause a significant reduction in the specific surface area of the glass powder, as measured by known procedures such as by a "Quantasorb" B.E.T. surface area analyzer. The reduction in specific surface area will be at least 50 per cent (i.e. the surface area of the heat treated glass powder will be less than one-half that of the untreated powder), up to 80 to 90 per cent, or even more in some cases. The heat treatment time is not at all critical in that it need be carried out only for the minimum time needed to heat all the powder to the desired temperature. Apparently, the effect of the heat on the glass powder is quite rapid, and all that is required is to bring all of the mass of powder up to the desired temperature. However, since the glass powder is an excellent heat insulator, this can take several hours for masses of powder wherein the heat must travel through a significant thickness of powder to heat all of the glass to the desired temperature.

The following is an illustration of a preferred heat treatment carried out on the barium glass used below in the Examples, and referred to as Filler A or Filler B:

The barium glass had the following composition:

SiO₂ 67 mole per cent

BaO—16.4 mole per cent

B₂O₃—10 mole per cent

Al₂O₃—6.6 mole per cent

The raw glass powder, prior to acid wash, has a specific surface area of about 0.8 ± 0.1 m²/gm. After acid-washing as described above, the specific surface area is about 10 ± 2 m²/gm.

Five kilograms of the acid-washed powder are placed in a sagger crucible. The crucible is cylindrical, about 30.5 cm (12 inches) in diameter and 25.4 cm (10 inches) high. Five kilograms of the powder nearly fill the crucible. The crucible containing the powder is placed in an oven, which is set at 650°C. It takes about 16 hours for the entire mass of powder to heat up to 650°C. After 16 hours, the furnace is turned off and the powder is slowly cooled to room temperature. The specific surface area of the heat treated glass is about 3.5 ± 1 m²/gm.

As is known in the art, a silane coupling agent can be employed to enhance the bond between the filler and the resin. Such coupling agents include gamma - methacryloxypropyltrimethoxysilane.

It is desirable to include a small percentage of colloidal silica in the composition in order to adjust the viscosity and the handling characteristics of the composite paste. For instance, from 2 to 25 weight per cent of colloidal silica, based on weight of the entire composite, is beneficial.

The colloidal silica is preferably treated with a silane coupling agent such as gamma - methacryloxypropyltrimethoxysilane ("A-174"). After such treatment, the silica should be protected from ambient moisture because it may absorb up to 1 weight per cent of water from the atmosphere, as measured by DSC.

In the examples, the following materials were used:

Bisphenol-A dimethacrylate ("BADM")

Ethoxylated bisphenol-A dimethacrylate ("EBDM")

Methacrylic acid ("MAA")

1,6-hexamethylene glycol dimethacrylate ("HMGDM")

2,2'-propane bis[3-(4-phenoxy)-2-hydroxypropyl-1 methacrylate] ("Bis-GMA")

Tetraethylene glycol dimethacrylate ("TEGDM")

2-(N,N-dimethylamino)ethyl methacrylate ("DMAEMA")

Ethyl 4-(N,N-dimethylamino)benzoate ("EDMAB")

Filler A—Conventional acid-washed 0—13 μm barium glass powder having the following particle size analysis (by Coulter Counter):

100% below 13 μm

55% below 5 μm

18% below 2 μm

Water content, by DSC, was 1.05 weight per cent

Filler B—Same 0—13 μm glass powder as Filler A, but heated to 650°C for sixteen hours as described above.

The water content, by DSC, was 0.05 weight per cent.

Filler C—Quartz powder (0—80 μm) having the following particle size analysis:

100% below 80—100 μm

50% below 13 μm

16% below 5 μm

The water content, by DSC, is below 0.01 weight per cent.

Filler D—Quartz powder (0—10 μm) having the following particle size analysis:

100% below 10 μm

77% below 5 μm

23% below 2 μm

Water content, by DSC, is below 0.01 weight per cent.

Filler E—0—90µm Barium glass powder heat treated at 650°C for 16 hours, having the following particle size analysis:

- 100% below 80—100µm
- 50% below 13µm
- 12% below 5µm

Water content, by DSC, is 0.025 weight per cent.

Filler F—0—5µm Quartz powder having the following particle size analysis:

- 100% below 5µm
- 70% below 1µm
- Average—0.66µm

Water content, by DSC, was 0.01 weight per cent.

Fillers A, C and E illustrate the prior art. Filler A is a hydrophilic filler and fillers C and E have particle sizes outside that specified in claim 1. Fillers B, D and F illustrate the present invention.

The water contents are determined on the fillers prior to treatment with silane. The quartz fillers were treated with 3.2 weight per cent A-174 silane (Union Carbide), and the barium glass fillers were treated with 1 weight per cent A-174 silane (gamma - methacryloxypropyl - trimethoxysilane).

Examples 1—2 and Controls 1—3

A series of filled resin systems, formulated to be useful as dental composites, were prepared. The composite formulations were prepared by mixing fillers into the resins using a mini-Hobart (drill) mixer until a smooth paste resulted. The pastes were then placed in a vacuum oven and de-gassed at about 533 Pa (4 mm mercury pressure) until they were void-free, as determined by microscopic examination. Flexural test samples were made by placing the uncured filled resins in "Teflon" (registered Trade Mark) molds between glass slides, and exposing each side to 60 seconds exposure from a 75 watt/12 volt quartz projector lamp. All samples were aged for 24 hours at 37°C in deionized water. Ten samples of each composite were tested for initial flexural strength, and ten additional samples were placed in pressure bottles with 300 ml of deionized water, and were held at about 506.5 kPa (5 atmospheres) and 145°C for 7 days. After this time, they were removed from the bottles and tested for flexural strength, using an Instron HP-11 stress-strain testing apparatus.

Table I displays the formulations and Table II displays the results of the flexural testing.

TABLE I

Resin A	Parts by weight
Bis-GMA	61.2
BADM	6.8
TEGDM	26.9
MAA	2.0
Benzil	0.3
Camphorquinone	0.3
DMAEMA	2.5
Viscosity—2.56 Pas(2560 cps)	
Water absorption ⁽¹⁾ —2.34 mg/cm ² (0.01) ⁽²⁾	
Resin B	
EBDM	96.9
Camphorquinone	0.3
Benzil	0.3
DMAEMA	2.5
Viscosity—2.24 Pas(2240 cps)	
Water Absorption—0.41 mg/cm ² (0.01)	
Resin C	
EBDM	84.55
HMGDM	12.6
Camphorquinone	0.25
DMAEMA	2.5
Viscosity—1.96 Pas(1960 cps)	
Water Absorption—0.80 mg/cm ²	
Resins B and C meet the requirements for resins set out in claim 1. However, resin A does not.	

⁽¹⁾ The water absorption was determined on the cured, unfilled resins by ADA Specification No.

27—immersion in water at 37°C for seven days.

⁽²⁾ The numbers in parantheses after the test data are the standard deviations.

Control 1	
Resin A	28
Filler A	72
Control 2	
Resin A	28
Filler B	72
Control 3	
Resin B	28
Filler A	72
Example 1	
Resin B	28
Filler B	72
Example 2	
Resin C	28
Filler B	72

TABLE II

Flexural strength				
Composite	Initial strength mPa	Pressure boiled 7 days	% Loss	Water absorption ⁽³⁾ mg/cm ² , 7 days at 37°C.
Control 1				
(hydrophilic resin)	111.0	30.4	72.6	1.23
(hydrophilic filler)	(13.4)	(7.9)		(0.03)
Control 2				
(hydrophilic resin)	108.3	46.4	56.2	1.07
(hydrophobic filler)	(10.6)	(8.9)		(0.03)
Control 3				
(hydrophobic resin)	109.6	66.7	39.1	0.44
(hydrophilic filler)	(13.7)	(9.9)		(0.03)
Example 1				
(hydrophobic resin)	111.6	78.6	29.6	0.29
(hydrophobic filler)	(10.7)	(9.9)		(0.02)
Example 2				
(hydrophobic resin)	109.2	91.4	16.3	—
(hydrophobic filler)	(13.2)	(9.2)		

⁽³⁾ Water absorption on the filled composites.

Controls 1, 2, and 3, each of which contained either a hydrophilic resin or a hydrophilic filler or both, had much lower retention of flexural strength after pressure boiling, than did Examples 1 and 2, which exemplify the invention.

Example 3

To illustrate the effect of particle size, 28 parts, by weight, of Resin B was mixed with 72 parts of Fillers C, D, E, and B, respectively. The composites were vacuum degassed and made into flexural test samples, as was described in Example 1. The flexural strengths were determined after aging for 24 hours in deionized water at 37°C. The results are displayed in Table III:

TABLE III

Flexural strength	
Filler	MPa
C (0—90 μ m quartz)	117.4 (8.7)
D (0—10 μ m quartz)	124.3 (11.7)
E (0—90 μ m Ba glass)	108.1 (7.3)
B (0—13 μ m Ba glass)	119.1 (7.7)

Examples 4 and 5

Two photocurable compositions designed for use as dental composites were made from the following formulations (Table IV):

TABLE IV

Example 4	Parts, by weight
Resin B	22.2
Filler D	66.8
Colloidal Silica ⁽⁴⁾	11.0
Example 5	
Resin B	21.6
Filler B	67.5
Colloidal Silica ⁽⁴⁾	10.9

⁽⁴⁾ Fumed silica treated with gamma-methacryloxypropyl trimethoxysilane. (Cab-O-Sil (Registered Trade Mark) "M-5", Cabot Corporation)

The compositions were vacuum degassed and cured by exposure to light, as described in Example 1.

Representative properties of these materials after curing as described in Example 1 are shown in Table V:

TABLE V

	Example	
	4	5
Compressive strength, mPa	354.1	357.7
Diametral tensile strength, mPa	64.9	61.4
Flexural modulus, mPa	10,956	9,650
Flexural strength, mPa	126.1	127.9
Rockwell F hardness	93	94
Water absorption, %	0.38	0.32
Translucency	passes ADA Spec 27	
Flexural strength, mPa	86	117
after pressure boiling 7 days at 145°C and 533 Pa (5 atmospheres)	(32% loss)	(8% loss)

To demonstrate the benefit of vacuum degassing to reduce voids, samples of the same formulations were cured without having been vacuum degassed, and were tested for flexural strength as described above in Example 1. The results were:

Example 4	99.5 mPa
Example 5	90.8 mPa

Example 6

The following dental composite formulation was prepared:

TABLE VI

Component	Parts by weight
EBDM	17.71
di-camphoroquinone	0.05
Benzil	0.024
EDMAB	0.216
Resin	18.000
Filler F	62
Colloidal silica ⁽⁵⁾	20

⁽⁵⁾ "OX-50", marketed by DeGussa; It is a fumed silica having a surface area of 50 m²/gm and an average particle size of 0.05 μ m. It is treated with 10 weight per cent A-174 silane and has a water absorption content, by DSC, after such treatment of 0.7—0.8 weight per cent.

The composite was prepared by the following procedure:

The resin is charged to a Hobart mixer, and the quartz and silica are added in six equal portions, with mixing, over a period of 1—1/2 hours. The mixture is then charged to a double planetary mixer, which is kept at an absolute pressure of 8.7 kPa (65 millimeters of mercury). The agitators in this mixer are run for about 20 seconds every 15 minutes; the mixture is kept in the mixer for 1-1/4 hours.

Samples were cured by exposure to light, as described in Example 1. The following physical properties were measured on the cured composite:

TABLE VII

Compressive strength, mPa	340 (49,000 psi)
Diametral tensile strength, mPa	67.6 (9,880 psi)
Flexural modulus, mPa	17,500
Flexural strength, mPa	134
Rockwell F hardness	101.2
Translucency	Passes ADA spec 27

In a dental composite, one of the important physical properties that has an effect on durability is flexural modulus. The flexural modulus of natural tooth enamel is of the order of 50,000 to 80,000 mPa. Where there is a large difference between the flexural moduli of natural enamel and the restoration, significant stresses can be encountered at the enamel/restoration interface.

One of the reasons that polymer-based dental composites may not function well in Class 2 restorations (i.e. on biting surfaces of molars) is the large disparity between their flexural moduli (which can be as low as 7000 mPa) and that of natural tooth enamel. While the inventor herein has observed isolated batches of conventional composite material whose flexural moduli have approached that of this Example 6, preferred embodiments of the restorative compositions of this invention are the first composite formulations that the inventor has seen whose properties, including flexural modulus, are consistently such that they are legitimate candidates for clinical evaluation as Class 2 restorative materials.

Claims

1. A dental restorative composition comprising:

(a) a polymerizable composition containing at least one compound having at least two olefinically unsaturated groups, wherein, when said polymerizable composition is polymerized in the unfilled state, the resulting cured material has a water absorption as determined by ADA Specification No. 27 at 37°C for one week, of less than 1 milligram per square centimeter;

(b) a polymerization initiator for said polymerizable composition; and

(c) a hydrophobic inorganic filler having a volume average particle size below 15 μm , at least 30 per cent of the particles of said filler having a size of less than 5 μm , said filler being present in an amount within the range of from 35 to 78 volume per cent, based on volume of said polymerizable composition plus said filler, and said filler being selected from acid-washed and heat treated barium or strontium glass, wherein the heat treatment is carried out at a temperature below the sintering temperature of the glass, and at a temperature and for a period of time sufficient to effect at least a 50% reduction in the specific surface area of the glass.

2. The dental restorative composition of claim 1 wherein said component (a) is at least one compound selected from $\text{C}_4\text{--C}_{12}$ alkanediol acrylate or methacrylate and alkoxylated bisphenol-A-acrylate or methacrylate.

3. The dental restorative composition of claim 1 or claim 2 wherein said component (a) includes ethoxylated bisphenol-A dimethacrylate.

4. The dental restorative composition of any one of Claims 1 to 3 wherein said component (a) includes 1,10-decamethylene diol dimethacrylate or 1,6-hexamethylene diol dimethacrylate.

5. The dental restorative composition of any one of Claims 1 to 4 wherein said composition includes colloidal silica.

6. The dental restorative composition of any one of Claims 1 to 5 wherein said hydrophobic inorganic filler is acid-washed and heat treated barium glass.

7. The composition of Claim 6 wherein the acid-washed and heat treated barium glass has the following approximate composition:

SiO_2 —67	mole per cent
BaO —16.4	mole per cent

B₂O₃—10 mole per cent
Al₂O₃—6.6 mole per cent

8. The composition of any one of Claims 1 to 7 wherein the polymerization initiator is photosensitive.

9. A method of preparing a composition according to any one of Claims 1 to 8 comprising mixing (a), (b), and (c).

Patentansprüche

1. Zahnersatzmaterial, umfassend

(a) eine polymerisierbare Zusammensetzung, die wenigstens eine Verbindung enthält, die wenigstens zwei olefinisch ungesättigte Gruppen aufweist, wobei, wenn diese polymerisierbare Zusammensetzung im nichtgefüllten Zustand polymerisiert wird, das gebildete gehärtete Material eine Wasserabsorption, bestimmt nach der ADA-Spezifikation Nr. 27 bei 37°C für eine Woche, von weniger als 1 Milligramm je Quadratzentimeter aufweist; (b) einen Polymerisationsinitiator für die genannte polymerisierbare Zusammensetzung; und (c) einen hydrophoben anorganischen Füllstoff mit einer auf das Volumen bezogenen mittleren Teilchengröße von unter 15 µm, wobei wenigstens 30% der Teilchen des Füllstoffes eine Größe von weniger als 5 µm aufweisen, welcher Füllstoff in einer Menge in einem Bereich von 35 bis 78 Vol.-%, bezogen auf das Volumen aus der genannten polymerisierbaren Zusammensetzung und dem genannten Füller, vorliegt und dieser Füller aus säuregewaschenem und wärmebehandeltem Barium- oder Strontiumglas ausgewählt ist, wobei die Wärmebehandlung bei einer Temperatur unter der Sintertemperatur des Glases und bei einer Temperatur und während einer Zeitspanne ausgeführt wird, die ausreicht, um eine wenigstens 50%ige Verminderung der spezifischen Oberfläche des Glases zu bewirken.

2. Zahnersatzmaterial nach Anspruch 1, worin die genannte Komponente (a) wenigstens eine Verbindung, ausgewählt unter C₄-C₁₂-Alkandiolacrylat oder -methacrylat und alkoxyliertem Bisphenol-A-acrylat oder -methacrylat, ist.

3. Zahnersatzmaterial nach Anspruch 1 oder 2, worin die genannte Komponente (a) alkoxyliertes Bisphenol-A-dimethacrylat umfaßt.

4. Zahnersatzmaterial nach einem der Ansprüche 1 bis 3, worin die genannte Komponente (a) 1,10-Decamethylen-diolmethacrylat oder 1,6-Hexamethylenoldimethacrylat umfaßt.

5. Zahnersatzmaterial nach einem der Ansprüche 1 bis 4, worin das Material kolloidale Kieselsäure umfaßt.

6. Zahnersatzmaterial nach einem der Ansprüche 1 bis 5, worin der genannte hydrophobe anorganische Füllstoff säuregewaschenes und wärmebehandeltes Bariumglas ist.

7. Material nach Anspruch 6, worin das säuregewaschene und wärmebehandelte Bariumglas die nachstehende annähernde Zusammensetzung aufweist:

SiO₂ - 67 Mol-%

BaO - 16,4 Mol-%

B₂O₃ - 10 Mol-%

Al₂O₃ - 6,6 Mol-%

8. Material nach einem der Ansprüche 1 bis 7, worin der Polymerisationsinitiator lichtempfindlich ist.

9. Verfahren zur Herstellung eines Materials nach einem der Ansprüche 1 bis 8, umfassend ein Vermischen von (a), (b) und (c).

Revendications

1. Composition restauratrice dentaire comprenant :

(a) une composition polymérisable comprenant au moins un composé ayant au moins deux groupes à insaturation oléfinique, dans laquelle, lorsque ladite composition polymérisable est polymérisée à l'état non chargé, le matériau durci résultant possède une absorption d'eau, telle que déterminée par la spécification ADA n°27 à 37°C pendant une semaine, de moins de un milligramme par centimètre carré ;

- (b) un initiateur de polymérisation pour ladite composition polymérisable ; et
 (c) une charge hydrophobe inorganique ayant une grosseur moyenne de particules en volume au-dessous de 15 μm , au moins 30 pour cent des particules de ladite charge ayant une grosseur de moins de 5 μm , ladite charge étant présente en une quantité comprise dans l'intervalle allant de 35 à 78 pour cent en volume, par rapport au volume de ladite composition polymérisable plus de ladite charge, et ladite charge étant sélectionnée parmi le verre de baryum ou de strontium lavé à l'acide et traité thermiquement, le traitement thermique étant effectué à une température au-dessous de la température de frittage du verre et à une température et pour une période de temps suffisante pour effectuer au moins une réduction de 50 pour cent de la surface spéculaire du verre.
2. Composition restauratrice dentaire selon la revendication 1, caractérisée en ce que ledit constituant (a) est au moins un composé choisi parmi un acrylate ou méthacrylate d'alcane en $\text{C}_4 - \text{C}_{12}$ -diol et un acrylate ou méthacrylate de bisphénol-A alcoxyté.
 3. Composition restauratrice dentaire selon la revendication 1 ou 2, caractérisée en ce que ledit constituant (a) comprend le diméthacrylate de bisphénol-A éthoxyté.
 4. Composition restauratrice dentaire selon l'une quelconque des revendications 1 à 3, caractérisée en ce que ledit constituant (a) comprend le diméthacrylate de 1,10-décaméthylène diol ou le diméthacrylate de 1,6-hexaméthylène diol.
 5. Composition restauratrice dentaire selon l'une quelconque des revendications 1 à 4, caractérisée en ce que ladite composition comprend la silice colloïdale.
 6. Composition restauratrice dentaire selon l'une quelconque des revendications 1 à 5, caractérisée en ce que ladite charge hydrophobe inorganique est du verre de baryum lavé à l'acide et traité thermiquement.
 7. Composition selon la revendication 6, caractérisée en ce que le verre de baryum lavé à l'acide et traité thermiquement a la composition approchée suivante:
 - SiO_2 - 67 pour cent en mole
 - BaO - 16,4 pour cent en mole
 - B_2O_3 - 10 pour cent en mole
 - Al_2O_3 - 6.6 pour cent en mole
 8. Composition selon l'une quelconque des revendications 1 à 7, caractérisée en ce que l'initiateur de polymérisation est photosensible.
 9. Procédé de préparation d'une composition selon l'une quelconque des revendications 1 à 8, qui comprend le mélange de (a), (b) et (c).